J. Mater. Environ. Sci. 5 (1) (2014) 231-236
ISSN : 2028-2508
CODEN: JMESCN

Transport of silver nanoparticles capped with different stabilizers in water saturated porous media

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Received 23 July 2013, Revised 11 Sept 2013, Accepted 11 Sept 2013
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Abstract

This study investigated the transport of citrate and polyvinylpyrrolidone (PVP) capped silver nanoparticles in water saturated sand column. Silver nanoparticles were synthesized using Tollens' method and coated with sodium citrate and PVP. Characterization particle size and zeta potential of silver nanoparticles was conducted by dynamic light scattering and zetasizer. Transport of silver nanoparticles was determined using an ICP-MS. The result of this study shows that PVP coated silver nanoparticles is more stable than citrate coated nanoparticles. The retention of silver nanoparticles in the sand packed column ranged from 25-99%, suggesting they are quite mobile in the porous media. Ionic strength plays an important role in the nanoparticle transport. High ionic strength influent water can result in an increase of nanoparticle retention.

Keywords: silver nanoparticles, Tollens' method, water saturated sand column, silver nanoparticle retention.

Introduction

Silver nanoparticles (AgNP) have been widely applied in household and industries [1-3]. It was reported that commercial products containing AgNPs accounts for more than 23% of all nanotechnology based commercial products worldwide [3,4]. Numerous commercial applications of AgNP are attributed to their antimicrobial properties [5-8]. AgNP can be synthesized using Tollens' method, which reduces ionic silver into the elemental form using reducing agents such as mono- or di- saccharides. The particle sizes of synthesized AgNP range from 10-200 nm depending on the strength of the reducing agents [9]. Due to the wide applications, AgNP became a potential environmental risk to environmental water systems and soil [3-5]. For example, release of AgNP can harm the naturally occurring microorganisms due to their antimicrobial properties [4]. Therefore, it is important to understand the environmental transport of AgNP. A small number of recent studies have investigated the fate and transport of nanoparticles in environmental water systems. For example, Zhang et al. have studied the changes of physicochemical properties of AgNPs in different water chemistry conditions [3,4]. Chinnapongse et al. and Zhang et al. have focused on explaining how different natural water conditions could influence the mobility of AgNP [3-5]. However, transport of AgNPs in the porous media was rarely studied. As a matter of fact, transport of AgNPs in the porous media can lead to an improved understanding of their potential environmental risk in soil and sediments.

Recent studies have only reported the transport and fate of different nanoparticles in water saturated media such as TiO_2 nanoparticles. Up to 90% nanoparticle recovery has found. It was reported that the transport of TiO_2 nanoparticles is related to the particle size of nanoparticles [5].

This study bridged the gap in understanding the transport and fate of AgNP in porous media. It investigated the effect of ionic strength on the transport of AgNP in water saturated sand column. Dynamic light scattering (DLS) and zetasizing techniques were used to characterize AgNP in terms of particle size and surface charges. ICP-MS was used to determine the concentration of effluent AgNP concentration. This study improves the understanding of AgNP transport in soil and sediments. It can be used as important reference for the environmental risk assessment of AgNP release in natural environment.

2. Materials and methods

2.1. nAg synthesis

AgNP was synthesized using Tollens method. The concentrations of the reactants were 1×10^{-3} M, 1×10^{-2} M and 5×10^{-3} M for $AgNO_3$, maltose and ammonia, respectively [3,4]. pH value of the reaction system was adjusted to 11.5 using NaOH. Then, sodium citrate and PVP was added separately as capping agent. Sodium citrate and PVP was used in this study because they are widely used by other scientist, which allows us to compare the experimental results [4]. The AgNP cleaning process follows the previous published procedure. In brief, the obtained AgNP were cleaned with deionized (DI) water using a 10 kDa molecular weight cut-off (NMWCO) ultrafiltration membrane (Millipore, Model 8200; NMWCO: 10,000). DLS was used to measure the particle size of AgNP using ZEN 3600 zetasizer manufactured by Malvern. ξ-potential of nAg was determined at 25 ^{0}C. Influent and effluent concentration of nAg was measured as total Ag by dissolving nAg in 2% nitric acid and measured by ICP-MS (X series, Thermo Elemental). TEM (transmission electron microscope) images of citrate and PVP coated AgNP were obtained using a JEOL 2100 TEM.

2.2 Transport of AgNP in water saturated sand column

DI water was used to measure the effect of different concentration on the transport of AgNP (10 mg/L) in porous media. The porosity of the sand in glass column ranges from 30% to 30.9%. To study the effect of ionic strength, $MgSO_4$ was added to adjust ionic strength from 1 to 100 mM.

A glass column (15×1 cm inner diameter) with Teflon end fittings was used. Sand was incrementally packed in the column and the porosity was measured gravimetrically. The packed column was rinsed with DI water 5 times and then passed with the prepared AgNP solutions with different dilutions. Influent and effluent AgNP concentration was measured. To measure the effect of different ionic strength on the transport of AgNP, AgNP suspension at a selected ionic strength was prepared and its particle size and surface charges were measured using DLS and zetasizer. The AgNP concentration in the influent and effluent was determined according to the above-mentioned procedures.

3. Results and discussion

3.1 Characterization of citrate and PVP coated AgNP

TEM images of citrate and PVP coated AgNP were obtained. The TEM images showed that AgNP were near spherical-shaped. The average particle sizes were 15.3 and 18.2 for citrate and PVP coated AgNP, respectively. The obtained results were in consistent with other studies that indicate the particle size of citrate and PVP coated AgNP were below 20 nm [4,5].

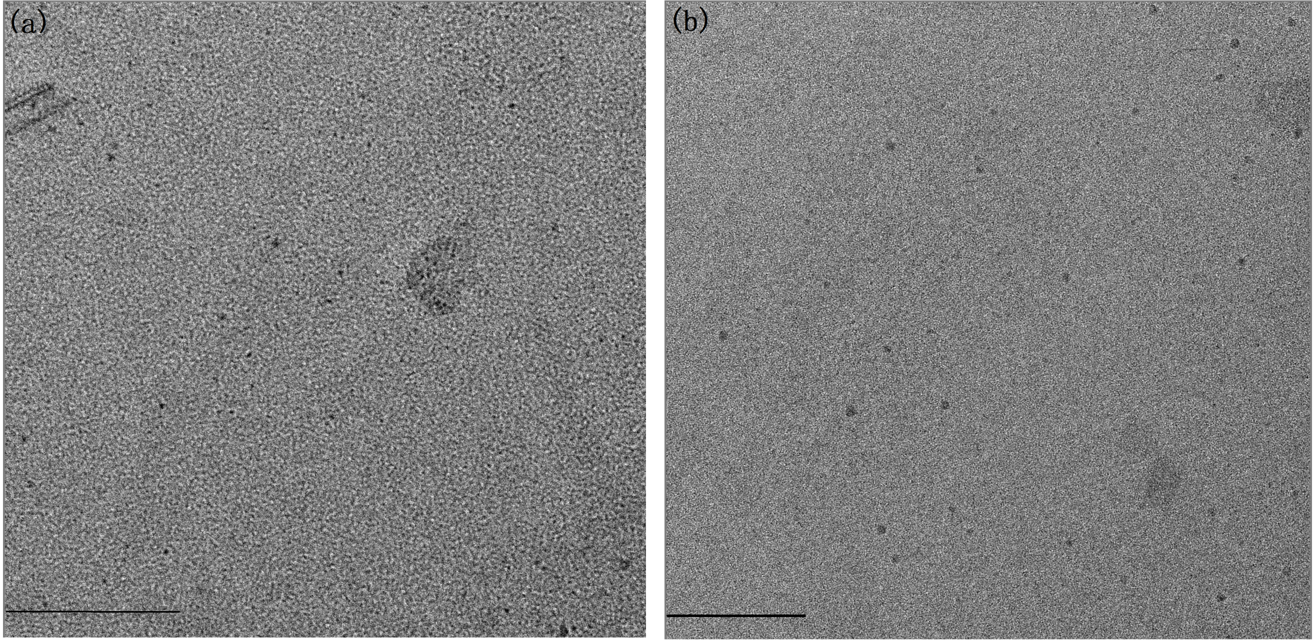

Figure 1. TEM images of citrate and PVP coated AgNP

3.2 Characterization of AgNP in different ionic strength

To simulate the potential fate of AgNP in different water conditions, particle size of AgNP was measured using dynamic light scattering technique. Stability of AgNP was measured in terms of zeta potential using a zetasizer. Shown in Fig. 2 and Fig. 3, increasing ionic strength can decrease the stability of AgNP. Li et al. (2010) indicated that aggregation rate of nanosilver without capping agent in both monovalent and divalent electrolyte solutions increased with increasing ionic strength [7]. Similarly results were observed by Huynh and Chen (2011) [10]. The observation was in consistent with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which indicates that the surface charge of AgNP can be neutralized by the introduced cations present in water that can reduce the repulsive energy barriers between nanoparticles [10]. The figures also show that PVP coated AgNP is more stable than citrate coated AgNP, which is mainly due to the adsorption mechanism of the two types of stabilizers. Citrate can coat on AgNP by electrostatic attraction [10-12]. However, increasing ionic strength can effectively remove the adsorbed citrate by neutralizing the charges of citrate [10-12]. On the contrary, PVP, a neutral organic stabilizer, can be coated on AgNP surface by regular adsorption, which is less sensitive to the surface charge screening processes by ionic strength than citrate. Meanwhile, PVP can introduce steric repulsion between nanoparticles, which is mainly attributed by the repulsion force generated by the steric configurations of PVP molecules [13-16].

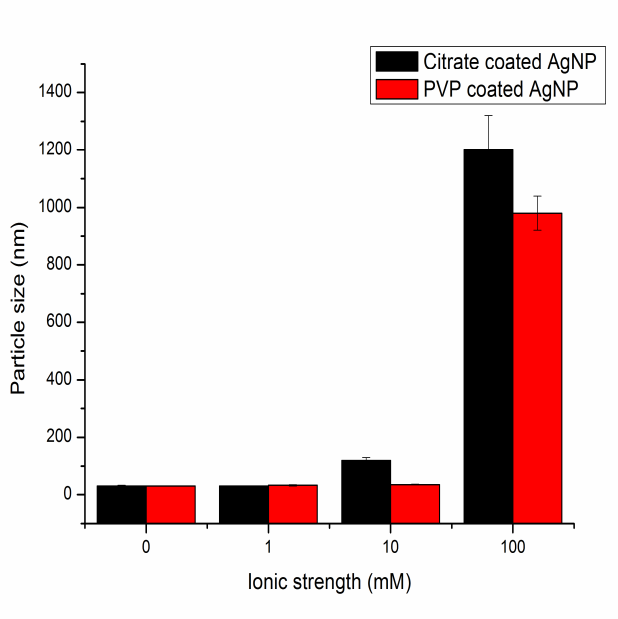

Figure 2. Particle size of AgNP in different ionic strength.

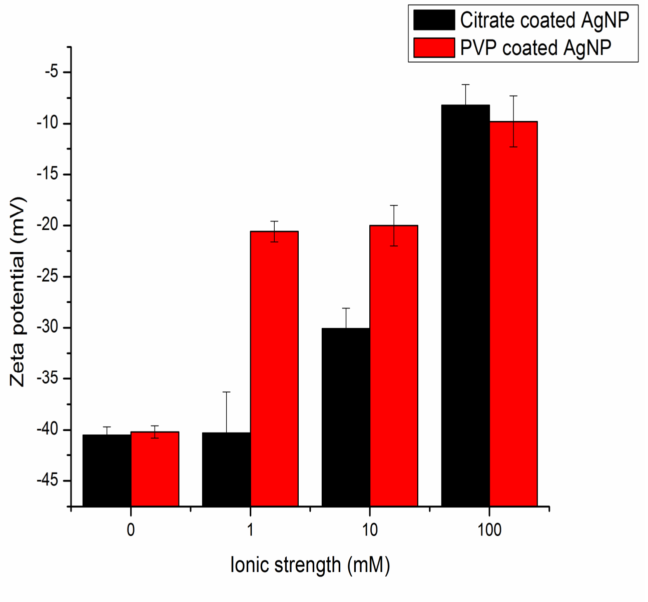

Figure 3. Zeta potential of AgNP in different ionic strength.

3.3 Transport of AgNP in water saturated sand column

Shown in Fig. 4 and Fig. 5, the percentages of AgNP retention in the sand column range from 25% to 99%. Ionic strength posed a strong effect on AgNP transport through the sand column. Our result can be explained by the increase in the particle size of AgNP. This observation is comparable to previous results for other types of nanoparticles and colloids [14-23]. Size exclusion is the main mechanism proposed to explain the retention of AgNP. Larger particles are more likely to be retained in porous media [12, 13]. In our case, high ionic strength can produce large AgNP aggregates [14-19]. This result is consistent with the size exclusion theory. However, ionic strength can also assist with the binding of AgNP onto sand material. As indicated in previous studies, sand material exhibits negative surface charge, which is the same as AgNP. As high ionic strength can reduce the surface charge of AgNP, it enhances the interaction between AgNP and the sand material [20-23], resulting in higher attachment efficiency. Our results also indicated that retention of PVP coated AgNP is more than citrate coated AgNP. This is because particle size of PVP coated nanoparticles is less sensitive to changes in ionic strength. The recovery of citrate and PVP coated AgNP was listed in Table 1. The recovery rate is in comparable with previous published results [20-23]. Particle size of citrate and PVP coated AgNP in the effluent was measured using DLS technique. After reacting with $MgSO_4$ and the adsorption process, large particles can be adsorbed or retained within the sand media by sorption and size exclusion process, leaving smaller nanoparticles released from the sand column. Fig. 6 indicated that particle size of AgNP in the effluent were smaller compared with the $MgSO_4$ treated AgNP. This indication was the first studied. It is of important significance to elucidate the transport process of AgNP in environmental porous media.

Table 1. Recovery of AgNP in different Ionic strength

Stabilizers	Ionic strength (mM)	Recovery (%)
Citrate	0	25.2
	10	49.2
	100	98.2
PVP	0	25.1
	10	40.2
	100	97.8

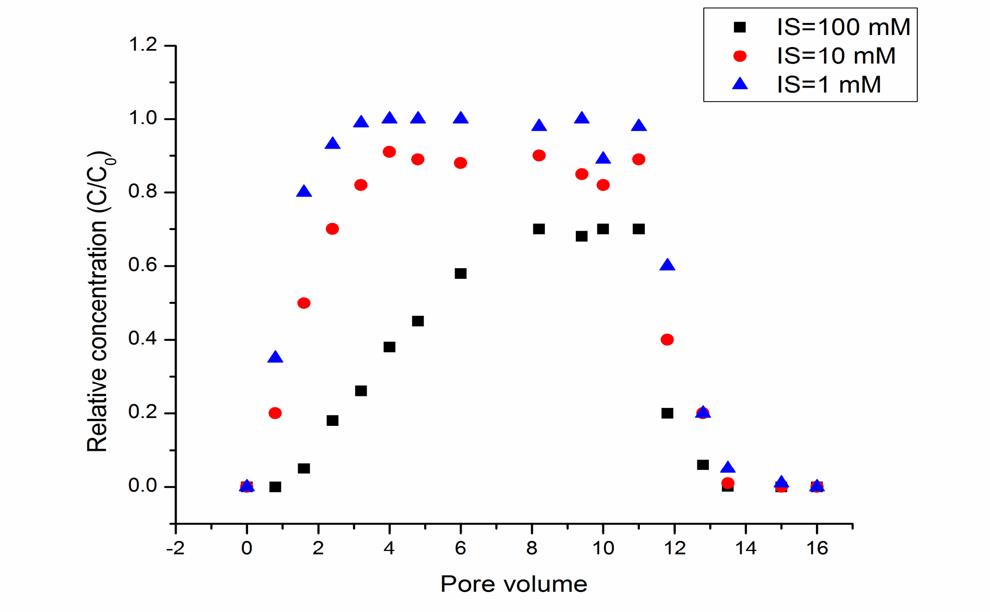

Figure 4. Transport of citrate coated AgNP in water saturated sand media using different ionic strength.

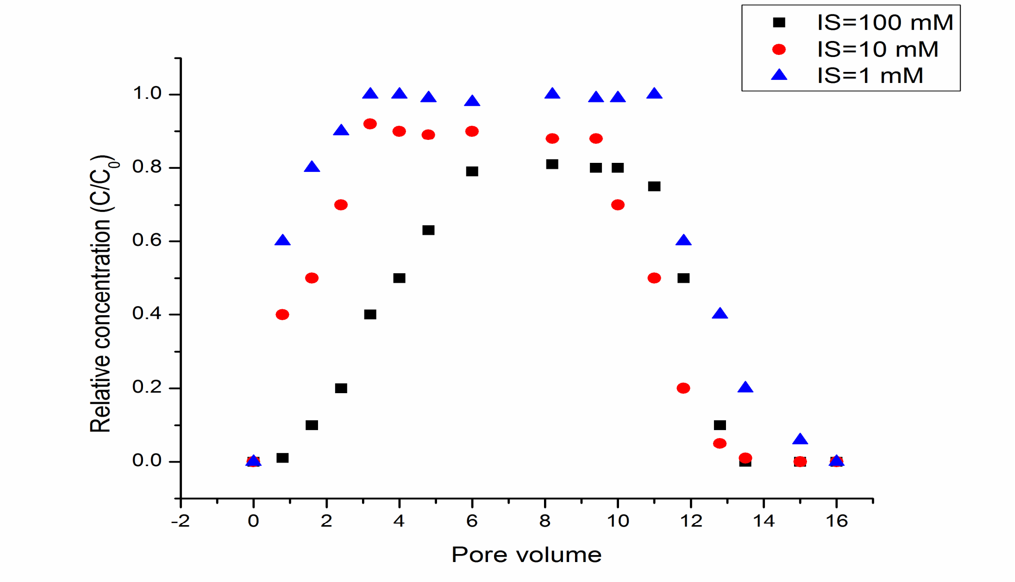

Figure 5. Transport of PVP coated AgNP in water saturated sand media using different ionic strength.

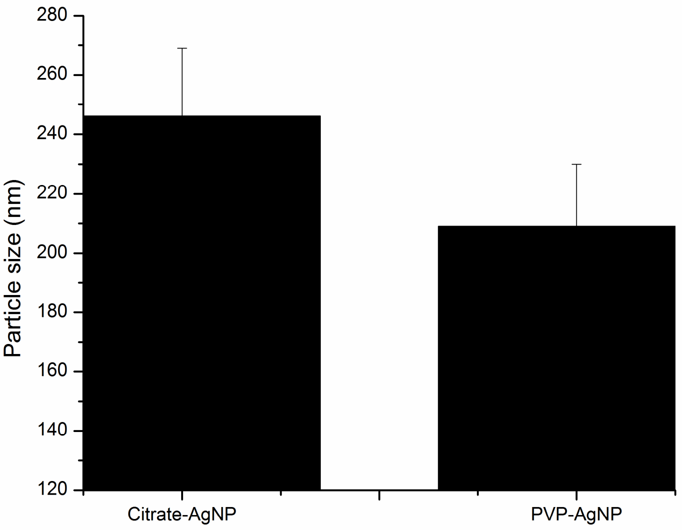

Figure 6. Particle size of citrate and PVP coated AgNP in the effluent (100 mM IS)

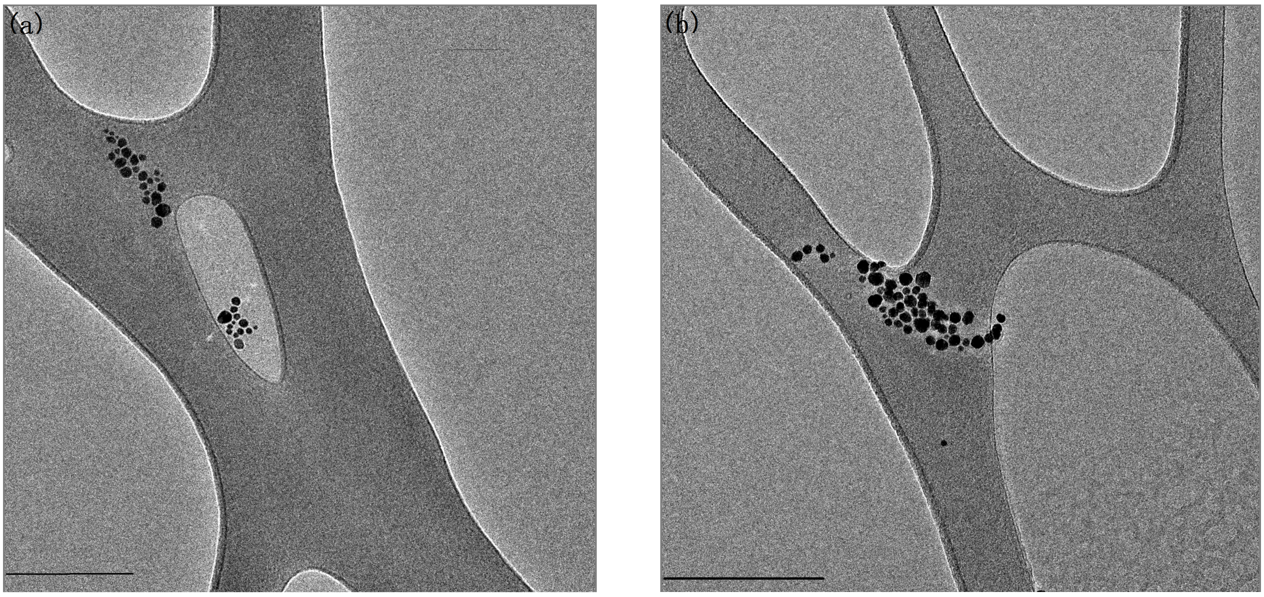

Figure 7. TEM image of citrate and PVP coated AgNP obtained from the effluent (100 mM IS, black line: 200 nm)

Conclusion

In this study, citrate and PVP coated AgNP was synthesized using Tollens method. DLS and zeta potential was used as two important parameters to characterize AgNP. Our result indicates that PVP coated AgNP is more stable than citrate coated AgNPs. Transport of AgNP was determined by comparing influent and effluent AgNP concentration. Our result suggests that increasing ionic strength can increase nanoparticle retention due to the aggregation of AgNP in high ionic strength. It is also found that less PVP stabilized AgNP was retained in comparison with citrate coated AgNPs. Finally, the particle size of citrate and PVP coated AgNP were measured and the TEM images were obtained. This study elucidated the transport of AgNP coated with different coatings. The obtained results can be served as reference for the risk assessment of AgNP release in natural porous media.

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(2014) ; http://www.jmaterenvironsci.com